High-resolution vacuum ultraviolet laser spectroscopy of molecules in a free supersonic jet: in search of rare CO isotopomers and CO–Ar van der Waals molecules

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Tunable vacuum ultraviolet radiation (in the range 142.7–146.7 nm) from a novel laser source was used to probe the electronic excitation spectrum of cold carbon monoxide molecules in a supersonic noble gas jet. Rotationally resolved spectra of $^{12}C^{16}O$, $^{13}C^{16}O$, as well as the rare but astronomically important $^{12}C^{18}O$ and $^{12}C^{17}O$ isotopomers, were recorded. Evidence was obtained for the formation of CO-containing van der Waals complexes in the jet.

Introduction

Laser spectroscopy is an extremely versatile and powerful tool in the investigation of molecules and molecular interactions. The combination of a frequency-tunable, narrow-band laser source with a free supersonic jet as sample offers particular advantages. In a supersonic jet a molecular gas can be studied under practically collision-free conditions, at very low temperature and with limited condensation. This simplifies the molecular spectrum, lowers the detection limit and facilitates the formation and spectroscopic study of weakly bound van der Waals complexes. In our experiment, carbon monoxide (CO) gas was investigated with the aim of detecting the rare but astrophysically important ^{17}O and ^{18}O isotopomers of CO and of investigating the formation of CO-containing van der Waals complexes in the jet.

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Experimental setup and method

The experimental setup, as discussed in more detail elsewhere,[1] is shown in Fig. 1. In the tunable vacuum ultraviolet (VUV) laser source that was developed in our laboratory, the radiation is generated by a nonlinear optical process, two-photon resonant four-wave sum-frequency mixing,[2] in a magnesium vapour-krypton gas medium prepared inside a heat pipe oven. The collinearly aligned beams of two excimer-pumped dye lasers (both Lambda Physik FL3001X with Coumarin 440 dye) were focused into the medium. One dye laser was tuned to a two-photon resonance of the magnesium vapour at 430.88 nm to optimize the VUV yield, and the second dye laser provided the tunability of the resulting VUV photons in the range 142.7–146.7 nm. Krypton gas was added to the medium to obtain phase matching, further enhancing the VUV yield.

The sample of CO gas, containing the isotopes of C and O in natural abundance, was mixed with argon or neon as carrier gas. The gas mixtures (containing 5–25% CO) were allowed to expand from a pressure of 4 bar through the 0.8-mm orifice of a pulsed valve (General Valves series 9) into a vacuum chamber kept at $\sim 5 \times 10^{-6}$ mbar by a turbo molecular pump (Pfeiffer TPH200). A delay generator (Stanford Research Systems DG535) was used to synchronize the gas and laser pulses.

A laser-induced fluorescence (LIF) spectrum was recorded by detecting the undispersed fluorescence from the irradiated volume in the jet by a solarblind photomultiplier (EMR Photoelectric 542G-08-18-03900) as a function of the VUV excitation wavelength. The photomultiplier was positioned perpendicular to the laser beam and the jet. The tuning of the laser and the data acquisition were controlled by a personal computer.

Results and discussion

Rotationally resolved VUV spectra of the singlet–singlet transitions from the $X^1\Sigma^+(v'' = 0)$ electronic ground state to the excited $A^1\Pi(v' = 3)$ vibronic state of CO were obtained. The known spectral lines[3] of $^{12}C^{16}O$ and $^{13}C^{16}O$ were used for wavelength calibration. The rotational temperatures were determined by fitting a Boltzmann distribution. By optimizing the experimental conditions, temperatures as low as 2 ± 1 K were obtained.

As shown in Fig. 2, the signal to noise ratio of the spectra was good enough to allow detection of six individual rotational lines of the rare $^{12}C^{17}O$ isotopomer and four lines of the $^{12}C^{18}O$ iso-

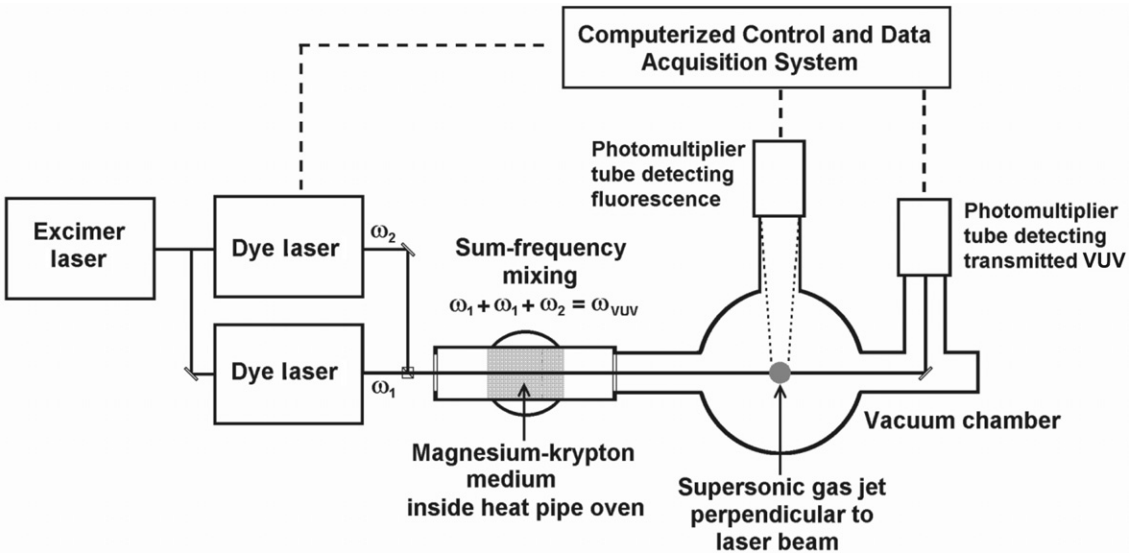

Fig. 1. Schematic illustration of the experimental layout of the VUV laser system and the fluorescence detection chamber.

topomer. Our results constituted the first rotationally resolved laboratory measurements of the A–X band of $^{12}C^{17}O$. This result shows the extreme sensitivity of our method, since the abundance of this isotopomer is only 0.04% in nature. A concentration of 3 parts per million could be detected. The new wavelength data on $^{12}C^{17}O$ were successfully applied to resolve a discrepancy in the interpretation of the astronomical observation of the VUV spectrum of interstellar $^{12}C^{17}O$ by Sheffer *et al.*[4] Our newly measured wavelength data resulted in consistent heliocentric velocity values.[5]

The temporal evolution of the gas pulse was recorded by fixing the excitation wavelength on a specific transition of $^{12}C^{16}O$ and changing the delay of the laser pulse relative to the gas pulse. Figure 3 shows the recorded time evolution of the 2.5-ms-long gas pulse. A dip was observed after the initial peak of the signal in that part of the gas pulse where the gas temperature was lowest. We interpret this as an indication that CO-containing van der Waals complexes were formed in the coldest part of the gas pulse, partially depleting the CO monomer population. When this phenomenon was investigated under a range of experimental conditions, a significant decrease in the CO monomer fluorescence signal was observed under conditions of high stagnation pressure (larger than 3 bar) with neon as carrier gas. As an increased stagnation pressure is expected to advance complex formation,[6] this is considered as further evidence of complexation of the CO monomers. However, the spectral features of such complexes have not been observed in the recorded fluorescence excitation spectra. Based on the dissociation dynamics of other dimer–noble gas complexes[7,8] and theoretical calculations on CO–Ar (M.C. Salazar and A.J. Hernández, unpubl. results), we consider complex-induced intersystem crossing or electronic predissociation as the most likely reasons for not detecting the fluorescence excitation spectrum of the CO-containing van der Waals complexes.

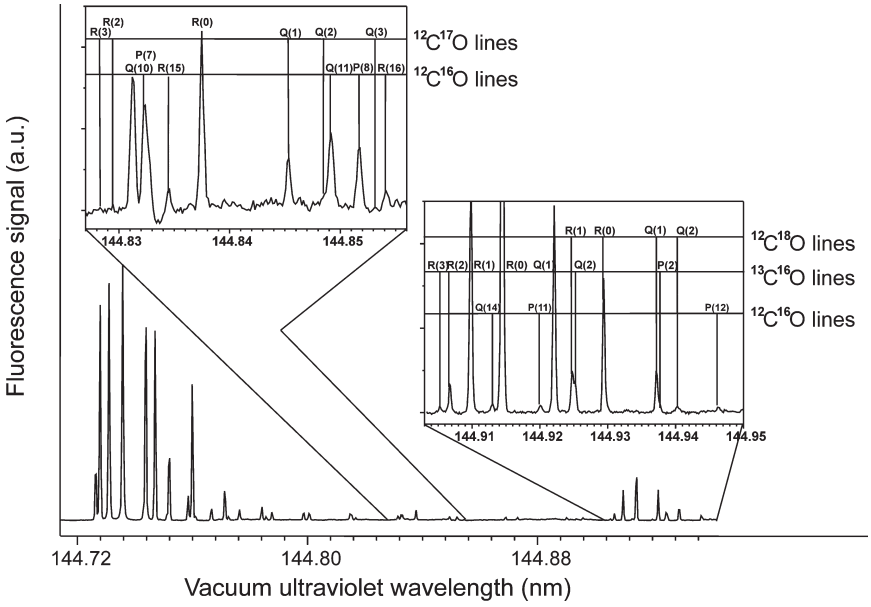

Fig. 2. The detailed spectrum of the rovibrational lines in natural CO, measured with 25% CO in Ar, and at 4 bar pressure.

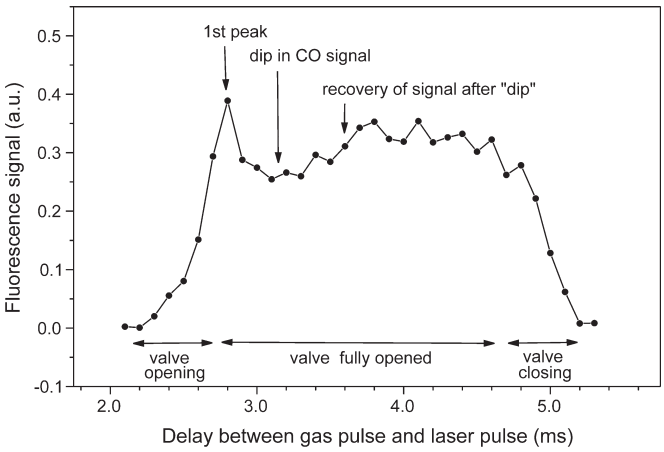

Fig. 3. The time evolution of the CO/Ar gas pulse. The graph shows the fluorescence signal of the CO monomer at various times after the pulsed valve was opened. The fluorescence signal of the R(0) line was recorded.

Conclusions

The combination of a narrow-bandwidth tunable laser source in the VUV and a free supersonic jet was demonstrated to facilitate high-resolution laser spectroscopy of CO molecules at temperatures down to ~2 K. The laser-induced fluorescence excitation spectra of rare $^{12}C^{17}O$ and $^{12}C^{18}O$ isotopomer species were detected, illustrating the low detection limit of the method and providing new spectral data for the $^{12}C^{17}O$ isotopomer. These data were relevant to a recent problem in astrophysics. Experimental evidence for complexation of CO in the supersonic jet has been obtained. The fluorescence excitation spectrum of the CO-containing complexes could not be observed, possibly due to complex-induced intersystem crossing or electronic predissociation.

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